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The Reduction of Selenate by Fulvic Acids in Soils of a High Gastric Cancer Risk Area in Sri Lanka*

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In order to elucidate the probable etiological factors for the incidence of gastric cancer, the interaction between selenate and fulvic acids was investigated under chemically controlled conditions. The reduction ability of selenate by fulvic acids was enhanced in acidic conditions. The fulvic acids may play an important role in the nitrosation process. Thus the investigations of the mechanism by which selenate interact with fulvic acids will provide a new insight into the chemical activation process by which selenium supplementation is supposed to act as an anticarcinogen.

KEY WORDS: Selenium, gastric cancer, redox potential, Sri Lanka.

INTRODUCTION

Previous epidemiological studies^{1,2} have shown that the northern and the western regions of Sri Lanka have an unusually high rate of gastric cancer. Compared to this, the rates of incidence of this condition in the other regions of the island is low. This extraordi-

^{*}Contribution from the Soil-Vegetation-Health Study Group.

nary geographical distribution of the disease strongly indicates that certain environmental factors may be involved in its etiology. Recent hydro-geochemical investigations^{2,3,4} have shown that high nitrate and high water soluble organic matter contents in potable waters are among a wide variety of etiological factors in the cancer introduction. In this study we have investigated the effects of fulvic acids, which form the soluble organic material in the soils, in the reduction of selenate. Information regarding the geochemical behaviour of fulvic acids in natural redox systems such as selenate/selenite is scarce.⁵ Although fulvic acids by themselves are not carcinogenic, they can be chemically activated by conversion to N-nitrosamines.⁶ The formation of nitrosamines normally takes place in dilute conditions⁷ and at elevated temperature levels.⁸ However, in the presence of organic matter, the reaction can proceed in natural non-acidic environments as well.⁶ It has been shown that fulvic acids as well as other organic matter, play a dominant role in the formation of Nnitrosamines by interacting with nitrites. The carcinogenic activity of N-nitrosamines in experimental rats has been known to be suppressed by selenium supplementation of their normal diets. The possible mechanism by which selenium could modulate carcinogenesis include effects on chemical activation, cellular proliferation or the ability to protect DNA from carcinogenic damage.9 Thus, an investigation of the interaction of selenate with fulvic acids will provide a new insight into the chemical activation process by which selenium supplementation is supposed to act as an anticarcinogen.

MATERIALS AND METHODS

The epidemiological data for the incidence of gastric cancer were obtained from the office of the Medical Statistician, Ministry of Health, Government of Sri Lanka, and the oxidizable organic matter data in potable waters were compiled from our previous reports.^{2,3}

Extraction of fulvic acids

The fulvic acids were extracted by a procedure as described by Melcer and Hassett.¹⁰ The soils used were from Nawalapitiya, an area in which the incidence of gastric cancer is endemic.^{1,2} Soil

samples were dried at 50° C, until at constant weight, visible plant tissue such as leaves and stems were removed and the samples passed through a 0.84 mm mesh sieve. Each sample was extracted three times with IL aliquots of 0.1 N NaOH for a total extracted time of 24 hours. Fulvic acids were extracted from humic acids and then purified.¹⁰

The effect of pH

In order to determine the effect of pH on the selenate reduction, 30 ppm Se as selenate solutions were mixed with 100 mg/L fulvic acid [FA] and the acidity of the final solution was adjusted [to pH 1–12] with a dilute acid/base.

The effect of reaction time

The effect of reaction time on reduction of selenate by fulvic acids was determined by testing two 100 mg/L selenate solutions at pH levels fo 1.80 and 8.00 for six intervals of time in the range of 4 hours to 2 days.

The effect of fulvic acid for selenate reduction

Fulvic acid was added in various amounts to aliquots of the 300 ppm Se as selenate solutions to achieve the concentrations in the range of 0 to 400 mg/L. The pH of the final solution was adjusted to 2.0 using a dilute acid.

Determination of Eh and selenite

The Eh measurements under different laboratory conditions were conducted in fulvic acid/selenate aqueous solutions after the equilibrium conditions had been reached. Before attaining the apparent equilibrium condition, the measurements of Eh fluctuates rapidly. This might imply that the heterogeneous redox kinetics of selenium oxyanions on the redox electrode are sluggish, resulting in the absence of a Nernstian electrode response. Thus the measurements of Eh tends to drift erratically with time. However, a near ideal reversibility and Nernstian response were observed after 72 hours, and the redox measurements were conducted with a pH meter (Model, 605 Metrom), after the apparent equilibrium conditions were attained. The selenite determinations were conducted fluoro-metrically using 2.3—diamino-napthalene (DAN) at 389 nm emission and 521 nm excitation wavelengths.¹¹

RESULTS

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Incidence of gastric cancer and fulvic acids in water

The association between the incidence of gastric cancer and the contents of oxidizable organic matter in drinking water¹² is as shown in Figure 1. The hypothesis, generated by this study, that high organic matter might be an etiological factor for gastric cancer was attractive, because of the evidence that fulvic and humic substances may enhance significantly the formation of N-nitro-samines. However, the exact role of fulvic acids in the nitrosation is not well understood, but it is interesting to note the fact that fulvic acids absorb a large range of the electromagnetic spectrum and they are known to contain free radicals.¹³ The nitrosamines can probably be formed under neutral conditions by free radical mechanism. The process is, however, more rapid in acidic aqueous solutions and occurs by a heterolytic mechanism.¹⁴ Selenate ion can block the formation of N-nitrosamines via oxidation of the functional groups of the fulvic acids yielding harmless products.

The reduction of selenate by fulvic acids

Since the predominant aqueous species of selenium under the condition of our experiments are selenite and selenate and the rate of reduction of selenate to selenite in solutions is too slow, the reduction capacity of selenate by fulvic acids was determined by measuring the amount of selenite formed. Figure 2 shows the concentration of selenite as a function of the pH in solutions containing 100 mg/L fulvic acids. The reduction ability of selenate by fulvic acids decreased with increase of pH, reaching an optimum condition at a pH of 1.80. A minimal reduction of selenate was found in neutral and alkaline solutions.



matter content in groundwater.

The time dependence of selenate reduction was studied at two acidic conditions (pH = 1.80 and pH = 8.00) and the results were as shown in Figure 3. The reduction rate of selenate was slow and it attained a plateau after 72 hours.

Figure 4 shows the results of the measurements of Eh with different concentrations of fulvic acids in 100 mg/L selenium as selenate solution of pH=1.80. Each data point in Figure 3 represents the mean of the values obtained at the end of an arbitrary five minutes of monitoring. The error bars for each point represent one standard deviation in the vertical direction, which is based on the variation in EMF for an arbitrary 3 runs after reaching the apparent equilibrium plateau. As shown in Figure 4, the trend of Eh was clearly downward, with the increase of fulvic acids content. This variation is largely controlled by the acidity of the solutions.

8



Reaction time Figure 3 The reduction of selenate by fulvic acids as a function of reaction time.

16

8

32

(hours)

72



Figure 4 The variation of redox potential (Eh) with the fulvic acid concentration. Vertical error bars indicate ± 1 standard deviation.

DISCUSSION AND SUMMARY

The fulvic acid molecules are believed to be large aromatic polymers with chemical properties determined largely by surface phenolic and carboxyl groups. These molecules differ from each other with respect to the number of functional groups and possibly the degree of aromaticity.¹⁵ The reduction mechanism of selenate to selenite by fulvic acids is not completely understood to date. Langford and Carey¹⁶ had observed important parallels between the way that illumination of a semiconductor can produce reactive species in solution and the reduction of oxyions by functional groups present in fulvic acids. The active sites that give irreversible oxidation are

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dominantly those which contain carboxyl and phenolic groups. After one electron oxidation the functional groups of fulvic acids can readily be decomposed by forming stable products such as CO_2 . In this way the back reaction of the redox system can easily be avoided.

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